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Electrical properties of ferromagnetic semiconducting single-walled carbon nanotubes

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Electrical properties of single-walled carbon nanotubes (SWCNTs) filled with Fe are studied by fabricating them as the channels of field-effect transistor devices. The synthesis of Fe-filled SWCNTs is realized by using ferrocene as the starting material. Our results reveal that ferrocene-filled SWCNTs show the interesting ambipolar behavior. In contrast, Fe-filled SWCNTs can exhibit high performance unipolar *n*-type semiconducting characteristics, suggesting the possibility of creating ferromagnetic semiconducting SWCNTs. Moreover, Coulomb blockade oscillations are significantly observed on Fe-filled SWCNTs, which indicates that they exhibit excellent single-electron transistor characteristics at low temperatures. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2337872]

Single-walled carbon nanotubes (SWCNTs) may provide one of the best replacement materials for molecular electronics because of their unique structural and electronic properties. A number of investigations on semiconducting SWCNTs have led to the development of field-effect transistors (FETs) and single-electron transistors (SETs).[1–3] Pristine SWCNTs are found to exhibit unipolar *p*-type behavior due to adsorption of oxygen on to the SWCNTs. While *n*-type SWCNT-FETs can be formed by doping a kind of impurity such as alkali metals or organic electron donors,[4–6] recent studies demonstrate that ambipolar nanotube FETs are also obtained by annealing or using nanotubes with larger diameters (small band gap) over 3 nm.[7,8] Thus, the current SWCNT-based devices generally utilize only the charge of conduction electrons. In addition to these charge dominated phenomena, SWCNTs also hold a considerable promise for applications in the field of electron spin due to their one-dimensional structure and ballistic transport properties. For example, spin-polarized transport properties of SWCNTs have been investigated by connecting them with two ferromagnetic electrodes in magnetic fields.[9] Therefore, it is quite natural to anticipate that the performance of SWCNT devices is further enhanced if both charge and spin of electrons can be used in SWCNTs themselves. One possible challenge to realize the above purpose is to inject ferromagnetic elements such as Fe, Co, or Ni into nonferromagnetic SWCNTs to make them magnetic. The biggest merit can be identified as that ferromagnetism and semiconductivity are expected to coexist in ferromagnetic semiconducting SWCNTs. However, although the theoretical studies indicate that SWCNTs filled with Fe can potentially be used as a natural candidate for spintronic devices,[10] such a kind of important and interesting topics has not yet been investigated experimentally.

In this letter, we report the synthesis of ferromagnetic semiconducting SWCNTs by Fe filling. We investigate the electronic transport properties of Fe-filled SWCNTs in comparison with those of ferrocene-filled SWCNTs and pristine SWCNTs. The results indicate that, compared with the *p*-type pristine SWCNTs and ambipolar ferrocene-filled SWCNTs, high performance unipolar *n*-type characteristics and regular Coulomb oscillations are observed for different samples of Fe-filled SWCNTs.

Pristine SWCNTs are prepared by an arc discharge using Fe/Ni as catalyst. The raw SWCNTs are purified by filtration and acid treatment[11] and placed in a glass ampoule together with excess solid ferrocene powder (about 1:20 by weight). The ampoule is evacuated and sealed, and then heated in an electronic furnace at 180 °C for 48 h. Ferrocene molecules are filled inside SWCNTs through above heating process, and samples with different filling levels can be obtained by changing the reaction time. For the synthesis of Fe-filled SWCNTs, samples of ferrocene-filled SWCNTs are first washed by alcohol to remove the excess ferrocene, and then annealed in vacuum at 700 °C for 30 min. As a result, the ferrocene molecules with diamagnetic property are decomposed and transformed into ferromagnetic Fe particles inside SWCNTs, which has been confirmed by a Quantum Design MPMS-5 superconducting quantum interference device magnetometer over a temperature range of 5–300 K. Figure 1 gives the transmission electron microscopy (TEM) images of individual SWCNTs for pristine (a), ferrocene filled (b), and Fe filled (c). Compared with the pristine SWCNT, Fig. 1(b) indicates clearly that ferrocene molecule clusters, as indicated by an arrow, have been filled inside a SWCNT with diameter of ~1.4 nm. In contrast, Fig. 1(c) reveals several Fe particles which are imaged as discrete dark spots (shown by arrows) in a SWCNT. In addition, the existence of Fe is

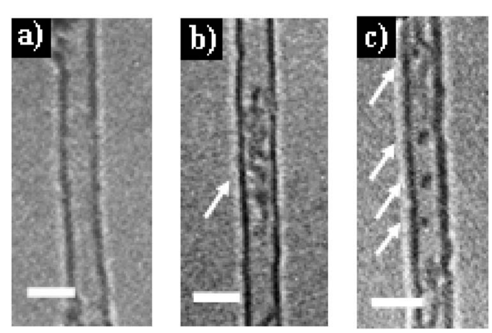

FIG. 1. TEM images of individual SWCNTs for pristine (a), ferrocene filled (b), and Fe filled (c) (scale bar: 2 nm).

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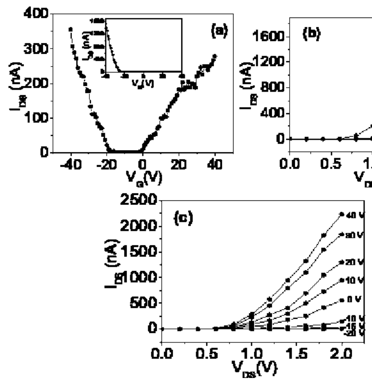

FIG. 2. Electrical transport properties of a ferrocene-filled SWCNT-FET. (a) Ambipolar transport characteristic at $V_{DS}=1$ V and the inset indicating a I_{DS}-V_G curve of a pristine SWCNT-FET measured at $V_{DS}=1$ V. (b) I_{DS}-V_{DS} characteristics under p channel. (c) I_{DS}-V_{DS} characteristics under n channel.

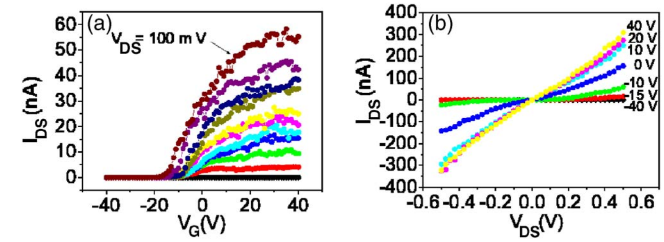

FIG. 3. (Color online) (a) I_{DS}-V_G curves for n-type Fe-filled SWCNTs measured at $V_{DS}=0-100$ mV in steps of 10 mV. (b) I_{DS}-V_{DS} characteristics for n-type Fe-filled SWCNT-FET.

further confirmed by energy dispersive x-ray spectrometry (Noran Instruments).

To fabricate SWCNT-FETs, different SWCNTs including pristine, ferrocene-filled, and Fe-filled SWCNTs are first dispersed by sonication in N,N-dimethylformamide (DMF) solvent, respectively, and then spin coated on different FET substrates which consist of beforehand prepared Au electrodes (thickness of 150 nm) placed on SiO_2 insulating layers (thickness of 500 nm). Each pair of Au electrodes is used as source and drain electrodes with a gap length of 500 nm between the two electrodes. A heavily doped Si substrate is used as a backgate which is prepared by Al evaporation. The excess DMF solution on the FET substrates is removed by a baking process at 400 K carried out in atmosphere for 30 min. Such kind of SWCNT-FETs has been made previously for investigating the electronic properties of SWCNTs encapsulating alkali metals in our laboratory.[12] Electronic transport properties of all SWCNT-FETs are measured using a semiconductor parameter analyzer (Agilent 4155C) in a vacuum condition.

Figure 2 gives typical electrical properties of a SWCNT-FET device fabricated with the ferrocene-filled SWCNTs. The characteristic of drain-source current versus gate voltage (I_{DS}-V_G) curve measured at room temperature for drain bias (V_{DS})=1 V is shown in Fig. 2(a). Obviously, compared with p-type pristine SWCNTs (shown in an inset), the device interestingly indicates ambipolar behavior. The region for $V_G < -20$ V on the left-hand region corresponds to p-type conduction, and n-type conductance is observed on the right-hand region for $V_G > 0$ V. An insulator region ($-20 < V_G < 0$ V) where the conductance shows three order decrease is found in between the p channel and the n channel. The conductance in both channels exhibits a symmetric feature, and the transconductance dI_{DS}/dV_G is similar for both channels in the linear I_{DS}-V_G regions. Figures 2(b) and 2(c) display the typical currents versus source-drain bias voltages (I_{DS}-V_{DS}) under various gate voltages in vacuum for p and n channels of the nanotube FET devices, respectively, and the conductance in both the channels indicates a strong gate voltage dependence. In Fig. 2(b) the negative gate voltages ranging from -40 to -20 V progressively reduce the linear conductance of the sample in marked contrast to its increase with increasing the positive gate voltage from -20 to 40 V for the n channel in Fig. 2(c), which is well in agreement with the typical ambipolar behavior of nanotube FET devices.

In contrast, after ferrocene molecules are decomposed inside SWCNTs, it is found that the semiconducting properties of SWCNTs are significantly changed as compared with ambipolar ferrocene-filled SWCNTs and p type of pristine SWCNTs. Figure 3(a) displays the I_{DS}-V_G characteristics for n-type Fe-filled SWCNTs with V_{DS} ranging from 0 to 100 mV in steps of 10 mV. The transfer characteristics confirm that the conductance of the Fe-filled SWCNT-FETs can well be controlled by the electrostatic potential in the channel. No ambipolar behavior, such as that observed for ferrocene-filled SWCNTs, is found in the whole gate voltage range from -40 to 40 V. Evidently, their n-type nature is attributed to the charge transfer between Fe atoms and local parts of SWCNTs, suggesting that ferromagnetic semiconducting SWCNTs can be formed by Fe filling. The threshold voltage (V_{th}) necessary to deplete the nanotube is about -15 V at 10 mV bias for the n-type Fe-filled SWCNTs, and the carrier (electron) concentration along the nanotube is estimated to be 3.3×10^7/cm according to Ref. 2. The mobility of carriers can be deduced to be 6.1 cm^2/V s from the slope $dI_{DS}/dV_G \sim 0.4\times10^{-9}$ A/V at $V_{DS}=10$ mV as determined from the linear region of I_{DS}-V_G curves. For comparison, this mobility is much higher than the average value of 1.5 cm^2/V s for most of p-type pristine SWCNTs measured under the same conditions. In addition, according to the comparison of the subthreshold swing (S) defined by $S = dV_G/d\log_{10} I_{DS}$,[13] it is estimated to be 5–10 V/decade and 1.1–2.7 V/decade for p-type and n-type SWCNT-FETs, respectively, which means that the n-type Fe-filled SWCNT-FETs exhibit a better performance than that of the pristine SWCNT-FETs in our experiments. Significantly, it is necessary to emphasize that a high on/off ratio $(I_{on}/I_{off}) \sim 10^6$ can almost be obtained at various bias voltages for the n-type SWCNTs, which is similar to the best value for n-type nanotube FETs fabricated with the metal-oxide-semiconductor field effect transistor geometry.[4] To further assess the performance of n-type SWCNT-FETs, we investigate the output characteristic of I_{DS}-V_{DS} curves with V_{DS} ranging from -0.5 to 0.5 V by applying different gate voltages from -40 to 40 V, as shown in Fig. 3(b). As expected, the conductance of sample is significantly suppressed by decreasing the gate voltages from 40 V until the gate voltage reaches about -15 V, which also exhibits a typical characteristic for n-type nanotube FETs. Moreover, by decreasing the reaction time of ferrocene and SWCNTs from 48 to 6 h, properties of Fe-filled SWCNTs at a low filling level turn out to be different from those shown in Figs. 3(a) and 3(b). Although the n-type characteristics remain in some Fe-filled SWCNTs at a low filling level, the threshold gate voltages for the n-type con-

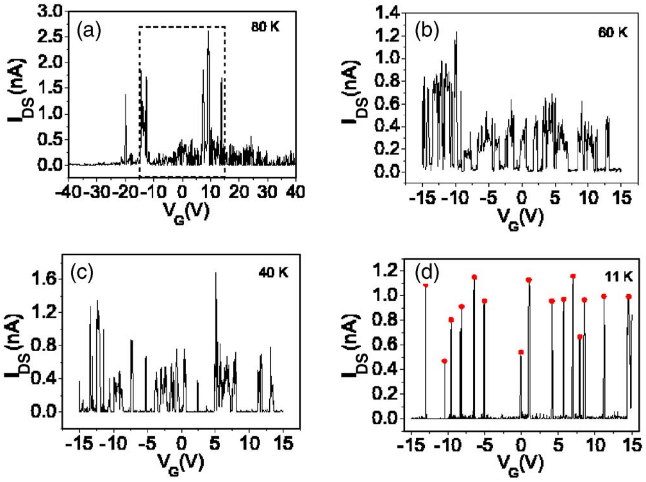

FIG. 4. I_{DS}-V_G characteristics of *n*-type Fe-filled SWCNTs at low temperatures: (a) Coulomb oscillation phenomenon begins to appear at 80 K. (b) and (c) indicate that the number of Coulomb oscillation peaks increases as the temperature is decreased down to 60 and 40 K, respectively. (d) A large number of regular sharp Coulomb oscillation peaks are observed at 11 K with a mean gate interval $\Delta V_G = 1.8$ V.

ductance tend to shift more positively (about −5 to 0 V) compared with those observed for *n*-type Fe-filled SWCNTs at a high filling level. In addition to the *n*-type SWCNTs, *p*-*n* junction can be created in SWCNTs due to Fe nanoparticles filled in part of SWCNTs, which seems to be related to the observations in the previous report.[14]

Temperature dependence measurements of the I_{DS}-V_G characteristics for *n*-type Fe-filled SWCNTs reveal that the curves become nonlinear and the conductance is dominated by a Coulomb blockade phenomenon with temperature cooled down to 11 K. Figure 4 shows the evolution of Coulomb oscillation peaks with temperature decreased from 80 to 11 K, which is measured with a small V_{DS} of 10 mV. It is noted that the Coulomb oscillations begin to appear at 80 K due to the decrease of conductance at low temperatures, as shown in Fig. 4(a). In addition, the number of current peaks is found to increase as the temperature is deceased from 80 to 60 and 40 K, as shown in Figs. 4(b) and 4(c) measured in the V_G range of −15 to 15 V, respectively. Significantly, when the temperature is cooled down to 11 K, a large number of sharp Coulomb oscillation peaks at regular intervals are strikingly observed in the large V_G range from −15 to 15 V, as described in Fig. 4(d), indicating a clear single-electron charging effect. The mean gate voltage period (ΔV_G) related to the energy for adding an additional electron to the quantum dot is measured to be 1.8 V, which has to be examined in view of the gate voltage efficiency in our case of the 500-nm-thick oxide backgate. Since the capacitance C_g between the quantum dot and rest of this system is estimated to be $C_g = e/\Delta V_G = 8.9 \times 10^{-19}$ F under the assumption of 10% efficiency, the gate capacitance per unit length is calculated to be 3.0×10^{-20} F/nm, which is given by $C/L \approx 2\pi\varepsilon\varepsilon_0/\ln(2h/r)$ according to the previous report.[2] Here ε, h, and r are the dielectric constant of SiO_2, thickness of oxide silicon layer, and radius of SWCNT, respectively, which are 3.9, 500 nm, and 0.7 nm. Therefore the average size of quantum dot in SWCNTs can roughly be estimated to be about 30 nm according to the description in the Refs. 15 and 16, which is much smaller than 500 nm of the tube length L between the two electrodes. The above results indicate that the Fe-filled SWCNTs can exhibit high performance FET characteristics at room temperature and interesting SET behavior at low temperatures.

It is to be emphasized that the FET characteristics of Fe-filled SWCNTs are notably different from those of ferrocene-filled SWCNTs which are used as the precursor for the formation of Fe-filled SWCNTs. The possible reason appears to be attributed to their different electron-donating abilities. As is well known, the fact that a ferrocene molecule contains a pair of six π-electron aromatic pentagonal carbon rings and six *d*-electron Fe atoms possibly makes it to act as a weak electron donor. In contrast, in the case of Fe-filled SWCNTs, the direct and relatively strong electron transfer from Fe atoms to SWCNTs may completely convert the *p*-type pristine SWCNTs into the *n*-type Fe-filled SWCNTs.

In conclusion, we have investigated the transport properties of Fe-filled SWCNTs by fabricating them as the channels of FET devices. The Fe-filled SWCNTs can exhibit the high performance *n*-type FET behavior and excellent SET characteristics at low temperatures. A shift toward a more positive threshold gate voltage is observed for *n*-type Fe-filled SWCNTs prepared at a low filling level. By comparison, ferrocene-filled SWCNTs show ambipolar FET behavior due to the weak donating ability of ferrocene.

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